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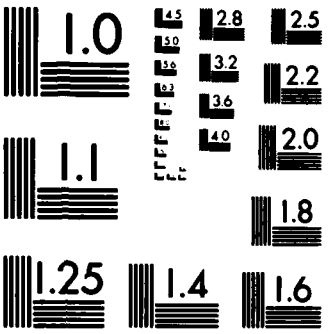

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High-temperature materials that exhibit small polaron conduction appear to exhibit the highest figures of merit. A thermoelectric model based on small polaron transport has been developed. The model predicts that broad-bandsemiconductors with small polarons hopping along inequivalent sites of distorted sublattices can result in increases in both the electrical conductivity and the Seebeck coefficient with increasing temperature without significant increases in thermal conductivity. High figures of merit (ZT), greater than 1 at 1000K, that increase with increasing temperatures are predicted. The model is being applied to the divalent metal containing (Y,LA)CrO(3) systems with an ABO(3) perovskite structure. Transport properties have been determined for various doping elements and for different compositions. These data are being used for the evaluation of this model.

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22a NAME OF RESPONSIBLE INDIVIDUAL
JOSEPH W HAGER

22b TELEPHONE NUMBER (Include Area Code)
(202) 767-4933

22c OFFICE SYMBOL

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RESEARCH PROGRESS AND FORECAST REPORT

ELECTRICAL AND THERMAL TRANSPORT PROPERTY STUDIES OF HIGH-TEMPERATURE THERMOELECTRIC MATERIALS

CONTRACT F-49620-83-0109 DEF

Battelle-Pacific Northwest Laboratories
Richland, Washington 99352

J. Lambert Bates
Program Manager

December 15, 1984

PROGRAM MANAGEMENT SUMMARY

High-temperature materials that exhibit small polaron conduction appear to exhibit the highest figures of merit. A thermoelectric model based on small polaron transport has been developed. The model predicts that broad-band semiconductors with small polarons hopping along inequivalent sites of distorted sublattices can result in increases in both the electrical conductivity and the Seebeck coefficient with increasing temperature without significant increases in thermal conductivity. High figures of merit (ZT), greater than 1 at 1000K, that increase with increasing temperature are predicted. The model is being applied to the divalent metal containing (Y,La)CrO_3 systems with an ABO_3 perovskite structure. Transport properties have been determined for various doping elements and for different compositions. These data are being used for the evaluation of this model.

The study of the transport properties for the In_2O_3-SnO_2 system was completed. Low values of the figure of merit were obtained as expected for these degenerate-type semiconductors.

Research will continue to emphasize the small-polaron thermoelectric model. To verify and refine the model, experimental transport measurement studies will emphasize the effects of substitutions in the ABO_3, especially the distorted lattice developed by substitution on B or O sites that increases inequivalent sites for hopping of small polarons. The model and experimental studies will be expanded to include the small-polaron conducting rare-earth oxysulfides and other oxychalcogenide materials.

OBJECTIVES

The objectives of this study are to determine limiting values for the figure of merit (ZT) and to establish a theoretical base for interpreting the experimental data for high-temperature thermoelectric materials.

THEORY

Efforts have concentrated on developing a model for thermoelectric properties of materials characterized by small polaron transport. Such a model should be useful for interpreting the experimental results for the perovskites now being studied, for calculating possible values for the figure of merit of small polaron conducting materials and eventually for establishing the theoretical and empirical limits to ZT for high-temperature thermoelectric materials. The theory for small polarons is being emphasized since the high-temperature materials that appear to have the best thermoelectric properties, such as boron carbide, rare-earth sulfides, conduct by this transport mechanism.

A small polaron refers to an electron state in a solid that is localized over a region of the order of a lattice constant. Each ion is surrounded by an electron cloud except the one located at the center where the orbital electron is missing. As a result, the outer electrons are attracted toward the center and the energy level of the electron state associated with the center ion is increased. The resultant hole--an absence of an electron--can move through the lattice, hopping between equivalent or inequivalent sites. In this transport process, energy is exchanged during hopping.

The present approach to developing a thermoelectric model for small polarons is the need for small polaron transport at "inequivalent sites" in a lattice. The electrical conductivity (σ) for small polaron transport is proportional to the product of the drift mobility and the carrier density. The values for the drift mobility are low. However, the electrical conductivity can be high since the density of carriers can be very large, approaching that of the atom density in the systems. This may occur because of the very high dopant levels in many oxide systems.

The Seebeck coefficient (S) is the average energy transferred by a carrier divided by T. S has two terms, one related to the location of the Fermi level (the carrier density) and the other dependent upon the nature of the hopping mechanism.

$$S = A + BT$$

The A term has always been included in past treatment of small-polaron transport, but only recently has the additional B term been considered. This additional term is important only if hopping occurs between inequivalent sites. This B term is very significant for thermoelectric materials since S will increase with increasing temperature. With the figure of merit proportional to $S^2\sigma T/\lambda$, small polaron conducting materials may exhibit significantly higher ZT values. In addition, these same materials continue to exhibit low thermal conductivities (λ), enhancing further the ZT values.

Calculations for small-polaron conducting materials, which include the effects of hopping between inequivalent sites, suggest that ZT values greater than 1.0 at 1000K are quite possible. These calculations assume for the perovskite (ABO_3) chromites, a thermal conductivity of 0.1 W/cm-K; a fraction (χ) of the A sites occupied by an atom with a valence one less than A to be greater than 0.1 and a finite value near 0.1 for the overlap integral (J). [The overlap integral for equivalent sites is 0.]

The model calculations suggest some ways to improve the figure of merit of the perovskite materials:

1) Increase the fraction (χ) of substitutions on the A sites to values between 0.2 and 0.4.
2) Establish inequivalent environments on the B sublattice to yield a finite value for J.

Some approaches that might accomplish these changes in the $La(M)CrO_3$ are to:

1) Increase the doping level of Sr, Ca, etc. to between 10 and 40% to replace the La in $LaCrO_3$.
2) Distort a large fraction of Cr sites with substitution on the Cr sublattice or on the O sublattice. For example:

   $(La_{1-x}\ Sr_x)\ (Cr_{1-y}\ W_y O_3)$ or $(La_{1-x}\ Sr_x)\ Cr\ O_{1-y}\ S_y)$
   with $x \sim 0.2$ to 0.4 and $y \sim 0.2$ to 0.4 or
   $(La_{1-x}\ Sr_x)\ (CrO_{1-y}\ V_y)$ with V = oxygen vacancy.

TRANSPORT PROPERTY STUDIES

Extensive electrical conductivity and Seebeck coefficient measurements were performed for In_2O_3-SnO_2, $ABO_3[(La,Y,Gd)_{0.98}Sr_{0.2}CrO_3$ and $Y(Ba,Sr,Ca,Mg)CrO_3]$ systems.

In_2O_3-SnO_2: The In_2O_3-SnO_2 system represents a degenerate, broad band semiconductor system with characteristic low Seebeck coefficients (-50 to -125 μV/K) and high electrical conductivities (>500 mhos/cm) resulting in low ZT values at 1600K of less than 0.1. The study of this system is complete and a paper is being prepared for publication.

ABO_3 Perovskite: The $(La,Y)CrO_3$ systems are being studied to provide data for verifying and refining the small-polaron thermoelectric model. Approximately 35 different compositions have been studied. These include $(Y,La)CrO_3$ containing divalent additions of Mg, Ca, Sr or Ba with systematic substitutions in composition to determine variations in σ and S, and the charge carrier mechanism in the system. Additions of Al and Fe have also been made for possible substitutions on the B site.

Small-polaron transport was determined to be the dominant charge carrier mechanism for these $(La,Y)CrO_3$ systems. Observed trends in the electrical transport properties for the ABO_3 systems have been developed relating to substitutional concentration, atomic radii and temperature. Increased carrier concentration (increased electrical conductivity) was obtained by increasing the M^{+2} substitution for the A site M^{+3} cation. These results support the currently accepted theory that charge compensatory carriers originate from the Cr^{+3} to Cr^{+4} transition on the B site and form polarons by interactions either at the B or O site or both. The current data suggest that distortion of the lattice due to interactions of electrons with the B or O site ions is a very short-range phenomenon. Thus, gross unit cell perturbations resulting from substitutions on the A site, result only in second order improvements to ZT. This tends to confirm the theory that the formation of inequivalent sites at the B and O sublattices are required for substantial changes in ZT.

Other Oxides: Preliminary transport properties have also been measured for La(Sr)MnO_3 and the HfO_2-RE_xO_y-In_2O_3 rhombohedral-bcc structures. The latter structure appears to be a degenerate-type semiconductor with low Seebeck coefficients.

Thermal Conductivity: Thermal conductivity measurements have been made for selected doped (La,Y)CrO_3 compositions in order to provide necessary data to calculate ZT. Since little variation in thermal conductivity are observed between the different compositions, it has not been necessary to conduct extensive measurements of the thermal diffusivity/conductivity.

Data Acquisition: All of the data are collected directly on computer systems with equations developed as a function of temperature for theoretical or experimental calculations of transport properties and ZT.

FUTURE DIRECTION

The work in the future will emphasize the development of the model for high-temperature thermoelectric materials with experimental transport measurements of small-polaron conducting materials made to verify and refine this model.

Theory: The theoretical study will continue the development of a high-temperature thermoelectric model based on small-polaron conduction along inequivalent sites. The influences of substitutions on the A and B sites in the (Y,La,Gd)CrO_3 perovskite structure will be emphasized. The experimental measurements will be evaluated using this model and more effort will be devoted to directing and to defining the experiments necessary for refining the model and for application to other high-temperature thermoelectric systems, such as the rare-earth oxysulfides

Experimental: Measurements for determining the substitutional effects on the A site in the ABO_3 perovskite system will be completed with emphasis on the (La,Y)(Sr)CrO_3 systems. The trends in transport properties related to atomic radii, structure, and concentration of substitutional atoms will be determined for application to the proposed model.

An important specific experiment is to develop a perovskite structure that is distorted at the Cr and/or O sublattices. Ta, W, Al, Mn, Co and Fe are being

considered for the Cr substitution. Sulfur is being considered for the O substitution.

New Materials: A study of the rare-earth oxysulfides with potentially high electrical conductivity and Seebeck coefficients will be initiated. The lanthanum sulfides are already being considered as a high-temperature thermoelectric material. The addition of oxygen to the sulfide is thought to improve thermal stability and thermoelectric properties. In addition, the results will also provide data for verifying and expanding the proposed model for small-polaron, high-temperature thermoelectric materials. Consideration will also be given to the oxyselenides, oxytellurides and other chalcogenide materials.

PUBLICATIONS

Two papers are being prepared and will be submitted for publication. These include: "Apparatus for High-Temperature Seebeck Coefficient Measurements" and "Electrical Transport Properties of In_2O_3-SnO_2."

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